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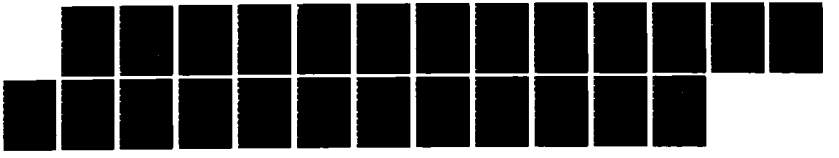

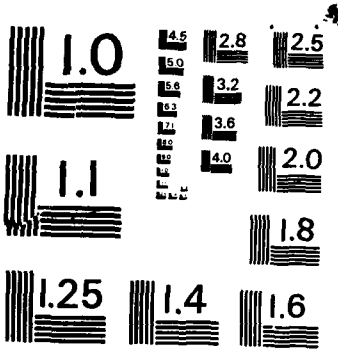

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TECHNICAL REPORT #3

TRANSPORT PROPERTIES OF LIQUID CRYSTAL DOPED FILMS OF POLYVINYLFERROCENE

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Liquid crystals, electrochemistry, transport, polyvinylferrocene

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The incorporation of the room temperature nematic phase 4-pentyl, 4'-cyanobiphenyl (K-15) into films of polyvinylferrocene is shown to substantially alter the rate of charge transport through the polymer film. The temperature dependance of the effect is especially dramatic above and below the nematic/isotropic transition temperature of K-15 (36°C). The observed effects are attributed to changes in the diffusion coefficient of the immobilized ferrocene groups due to changes in the viscosity of the film as well as to aggregation. In some cases, a split ferrocene wave was observed and this was attributed to

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20. Abstract continued

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TRANSPORT PROPERTIES OF LIQUID CRYSTAL DOPED FILMS OF POLYVINYLFERROCENE

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Abstract: The incorporation of the room temperature nematic phase 4-pentyl,4'-cyano-biphenyl (K-15) into films of polyvinylferrocene is shown to substantially alter the rate of charge transport through the polymer film. The temperature dependance of the effect is especially dramatic above and below the nematic/isotropic transition temperature of K-15 (36°C). The observed effects are attributed to changes in the diffusion coefficient of the immobilized ferrocene groups due to changes in the viscosity of the film as well as to aggregation. In some cases, a split ferrocene wave was observed and this was attributed to aggregation effects of the ferrocene sites with K-15. At K-15 concentrations below 1.3mM the data indicates a 1:2 K-15/ferrocene aggregate and 1:1 at higher K-15 concentrations. Keywords: Electrochemistry

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Introduction:

The deliberate and predictable control of the interfacial properties of electrochemical systems is at the heart of much of the modified electrode research. [1] A large number of systems have been employed with polymeric materials receiving the most attention in the recent past.[2] The control of the interfacial properties of electrodes can be achieved through surface modification by altering the nature of the immobilized redox active reagents, the microstructure of the deposit, the spatial distribution of sites, the transport properties of the medium and others.

We recently began a study of the electrochemical response of a number of redox materials dissolved in highly structured solvent media such as liquid crystals. [3] Our interest in this area arises from the possibility of controlling the structure of the solvent in the vicinity of the electrode surface (e.g. orientation of the solvent), as well as other solvent properties such as viscosity, by temperature variations. We recently completed an extensive characterization of, and electrochemical studies in, a series of room temperature nematic phases (liquid crystals) and found a range of effects attributable to solvent properties such as viscosity and dielectric constant and their temperature dependance.

From our ongoing interest in chemically modified electrodes and their applications,[4-7] we have begun a study of the effects of liquid crystalline dopants on the electrochemical response of

electrodes modified with electroactive polymer films. This is an area that has until recently [8] received very little attention, although it potentially represents a new way in which to alter interfacial reactivity.

We present some preliminary findings on studies of the electrochemical behavior of polyvinylferrocene films doped with varying concentrations of 4-pentyl,4'-cyano-biphenyl (K-15) and at temperatures above and below the nematic/isotropic transition.

Experimental:

Polyvinylferocene was prepared by free radical polymerization of vinylferrocene (Strem Chemicals) using azobisisobutyronitrile (AIBN) as initiator and benzene as solvent. A pyrex ampoule was charged with the benzene solution containing the monomer and initiator and deaerated in a vacuum line via three freeze/pump/thaw cycles. The polymerization was carried out in a water bath at 70°C for 72 hrs. after which the ampoule was opened and the polymer precipitated by the addition of ether. The polymer was purified by three recrystallizations from benzene/ether.

Methylene chloride (Burdick and Jackson distilled in glass) was used as received. Water was purified by passage through a Hydro water purification train. Potassium perchlorate (G.F. Smith) was recrystallized three times from purified water and vacuum dried at 90°C for 48 hrs. Tetra-n-butyl ammonium

perchlorate (TBAP, Southwestern Analytical) was recrystallized three times from ethyl acetate and vacuum dried at 70°C for 72 hrs. K-15 (4-pentyl, 4'-cyano-biphenyl) (E.M. Chemicals) was used as received. All other materials were of at least reagent grade quality and were used without further purification.

Electrochemical experiments were performed using an I.B.M. model EC 225 voltammetric analyzer, a Bioanalytical Systems Model 100, a Princeton Applied Research model 173 potentiostat and model 175 Universal Programmer or a locally built signal generator and potentiostat. Chronocoulometric experiments were performed on the B.A.S. 100 and the data analyzed on an I.B.M. PC AT computer. Conventional three compartment electrochemical cells with a glass jacket for temperature control were employed. A VWR model 1120 water circulator was employed for temperature control ($\pm$ 0.2°C). All potentials are referenced to the sodium saturated calomel electrode (SSCE) without regards for the liquid junction.

Procedure:

A platinum electrode (0.034cm^2) sealed in glass was employed. Prior to use, it was polished with 1 micron diamond paste (Buehler), rinsed with water, and acetone and placed in an ultrasonic cleaner (in acetone) for 30 seconds. Afterwards, they were rinsed with acetone.

Electrodes were modified with polyvinylferocene by electrodeposition from methylene chloride solution containing 0.1

M TBAP as supporting electrolyte. (When incorporation of K-15 was desired, the appropriate amount of K-15 was added to the depositon solution.) Each sample was prepared with 1.0mL of a polyvinylferrocene stock solution (0.04% wt/wt) and the appropriate amounts of K-15, methylene chloride and TBAP to give a final volume of 4 mL. Typical coverages of polyvinylferocene ranged from 2-4 $x10^{-8}$ moles/cm^2. After deposition, the electrode was removed from the cell, blotted of excess solution and placed in aqueous 0.1M potassium perchlorate electrolyte. The electrode was cycled at 50mV/s in the range of 0.0 to +0.80 V until a stable response was obtained. The electrochemical response at 45°C was obtained first, and the room temperature response obtained afterwards. (For room temperature experiments, the electrode was allowed to stand in a separate aqueous electrolyte bath for a period of 30 minutes to ensure equilibration.)

Results and discussion:

The electrochemical response of electrodes modified with polyvinylferocene (pvf) has been investigated in a wide range of solvents and supporting electrolytes and a number of different responses have been observed. [9] Under our experimental conditions we typically observe very well behaved cyclic voltammograms for electrodes modified with pvf. A typical response at room temperature is shown in Figure 1A where it can be seen that the anodic branch of the voltammogram is

significantly sharper than the the cathodic counterpart, however, the charge under both waves is essentially the same. This type of behavior has been reported previously.[10,11] At 45°C,(Figure 1B) the voltammetric response is only slightly altered; the main differences being a slight increase in the peak currents (and integrated areas) as well as a sharpening of both the anodic and cathodic waves. At both temperatures, the peak current increased linearly with sweep rate up to a rate of 200 mV/s. At higher values, there was a square root dependance of the peak current with sweep rate, typical of diffusion controlled processes. This type of transition has also been previously documented for polyvinylferrocene and other materials.[8-10]

In order to assess the effect of K-15 incorporated in to the pvf layer, the stability of the modified electrodes was determined at 25 and 45 °C in aqueous potassium perchlorate electrolyte. Aqueous electrolytes were employed in the voltammetric studies in order to ensure that the K-15 would not leach away from the electrode (due to the very low solubility of K-15 in water).

We found that voltammetric experiments at 25°C gave larger differences (when compared to results at 45°C) if the modified electrode was previously cycled at 45°C. Additionally, we expect that cooling of the K-15 doped modified electrodes (from isotropic K-15 to nematic K-15) should give a more reproducible surface than preparation by deposition alone. It is

for these reasons that we examined each electrode at 45°C initially, and then at 25°C.

As can be seen in Table I, the pvf films without K-15 were extremely stable at both temperatures with differences of less than 4% after one hour. In the presence of K-15, the films were not as stable, but even here, the differences were less than 8%.

We also monitored the formal potential for the ferrocene wave (taken as the average of the anodic and cathodic peak potentials) under these conditions and the results are presented in Table II. There are two trends worth noting. First of all there is a monotonic increase in the $E^{o'}$ value at both temperatures and secondly, the difference in the formal potentials at the two temperatures remains relatively insensitve to the K-15 concentration up to 0.1 mM but then decreases significantly and eventually the difference changes sign at a K-15 concentration of 16mM. We are inclined to ascribe these effects to specific ferrocene/K-15 interactions which might change the solvation environment and lead to changes in the formal potential. This is supported by the fact that a plot of $E^{o'}$ vs. log [K-15] (Figure 2) is linear (r=0.98) and from the slope, a ratio of K-15 to ferrocene of 0.5 can be derived. This lends strong support to the formation of a 1:2 adduct between K-15 and ferrocene. Close inspection of the plot, however, reveals the presence of two linear segments. The first one is at K-15 concentrations below about 3mM and the second at higher

values. In the first case the data indicate a 1:2 K-15:ferrocene complex as previously stated and in the latter a 1:1 complex appears to form. (This assignment is less definitive due to the scarcity of data in this region.) At K-15 concentrations above 16mM, the the current response and the film were unstable. Nonetheless, there is clear evidence for a specific K-15/ferrocene interaction.

The presence of K-15 within the polymer film also had some dramatic effects on the observed electrochemical response at 24 vs 45 ^{o}C. The effects on the peak current and integrated area are shown in Table III. The percent differences of cathodic peak currents as well as the integrated areas under the cathodic wave at 45 vs. 25 ^{o}C remain relatively insensitive to the K-15 concentration up to 0.1 mM. That is, these ratios do not differ significantly from those obtained in the absence of K-15. At K-15 concentrations of 1.3 mM and above, the differences become significant and at 16 mM K-15, the differences in the peak currents and integrated areas reach values as high as 52 and 40 percent respectively. Figure 3 shows representative voltammograms (at 25°C; (A) and 45°C; (B)) for pvf films with K-15 at a concentration of 16mM. It is worth noting that these changes follow the same pattern as the changes in the formal potentials, pointing perhaps to a mechanism that requires a minimum K-15 concentration in order to make the effect evident.

A similar trend is observed for the ratio of diffusion coefficients. At low K-15 concentration, the ratio remains

relatively constant, but at K-15 concentrations above 1.3mM significant differences are encountered. These effects are consistent with the aggregate formation alluded to previously.

There were also some truly dramatic effects in the observed voltammetric response. These are shown in Figure 4. The anodic wave of ferrocene is clearly split into two sharp peaks and furthermore the relative heights of the peaks change with temperature. At 25 ^{o}C the less positive peak is the dominant one, whereas at 45 ^{o}C, the more positive one is. This process is quite reversible; that is the relative heights of the peaks can be changed back and forth by changes in the temperature of the medium This seems to indicate that within the polymer film there are some very specific ferrocene K-15 interactions to form discrete species such as the aggregates mentioned previously with very different redox potentials. These two species appear to be in reversible equilibrium and the energy differences are such that dramatic changes in the population of these states can be achieved by these temperature changes.

We are now in the process of investigating this effect with a range of other redox materials whose geometric structure is such that large specific effects can be anticipated (e.g. TCNQ, TTF and others). We hope that by predictably controlling these effects, we might be able to achieve more specific control of the interfacial reactivity of modified electrodes.

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Table I

Stability of pvf modified electrodes in the presence and absence of K-15 and at 24 and 45 °C (% difference)

A. PVF without K-15

Tepm.(°C)	Time elapsed(min.)	ip_a	$Area_a$	i_{p_c}	$Area_c$
24.0	30	0.3	0.8	0.4	0.7
24.0	60	1.1	1.4	0.9	1.3
45.2	30	1.3	3.0	0.1	0.3
45.2	60	3.5	0.1	1.0	0.4

B. PVF with K-15 (1.3 mM)

Tepm.(°C)	Time elapsed(min.)	ip_a	$Area_a$	i_{p_c}	$Area_c$
45.1	30	0.4	6.9	2.9	3.3
45.1	60	2.6	7.8	6.9	6.2

Table II

Variation of Formal Potential as a Function of

K-15 Concentration and Temperature

[K-15](mM)	$E^{o'}$(45°C)(mV)	$E^{o'}$(24°C)(mV)	$E^{o'}$(45-24 °C)(mV)
16.0	+370	+379	-9
8.0	+363	+362	+1
1.3	+350	+336	+14
0.106	+337	+318	+19
0.0636	+331	+302	+29
0.0106	+326	+305	+21
0.0000	+327	+306	+21

Table III

Percent Difference in I_{pc} and $Area_c$ as a Function of K-15 Concentration and at Two Temperatures

[K-15](mM)	%Diff. I_{pc}	%Diff. $Area_c$
16.0	41.5	33.8
	52.2	40.4
	40.9	35.4
	41.8	31.8
8.0	36.6	17.2
	31.0	22.1
	29.3	16.1
	32.6	28.1
1.3	21.6	12.8
	19.5	12.0
	20.7	14.7
	18.5	9.4
0.106	18.0	8.4
	16.7	9.1
	14.7	6.8
	18.4	9.3

0.0636	15.6	6.6

Table III con't.

	16.1	6.4
	15.5	8.6
	13.6	4.3
0.0106	13.7	3.6
	12.1	3.7
	13.2	3.7
	12.9	2.9
0.000	14.6	6.1
	13.0	5.8
	13.1	4.4
	13.6	7.0
	14.1	6.2

Figure Legends:

Figure 1. Cyclic voltammograms of a pvf modified electrode at 50 mV/s in aqueous 0.1 $KClO_4$ at 25 ^{o}C; (A)(—) and 45 ^{o}C; (B)(•••).

Figure 2. Plot of $E^{o'}$ (at 45 ^{o}C) vs. log[K-15]

Figure 3. Cyclic voltammograms of a pvf/15mM K-15 modified electrode at 50 mV/s in aqueous 0.1M $KClO_4$ at 25°C; (A)(—) and 50 ^{o}C; (B)(•••).

Figure 4. Cyclic voltammograms of a pvf/1.3mM K-15 modified electrode at 10mV/s in aqueous 0.1M $KClO_4$ at 25 ^{o}C; (A)(——) and 50 ^{o}C; (B)(••).

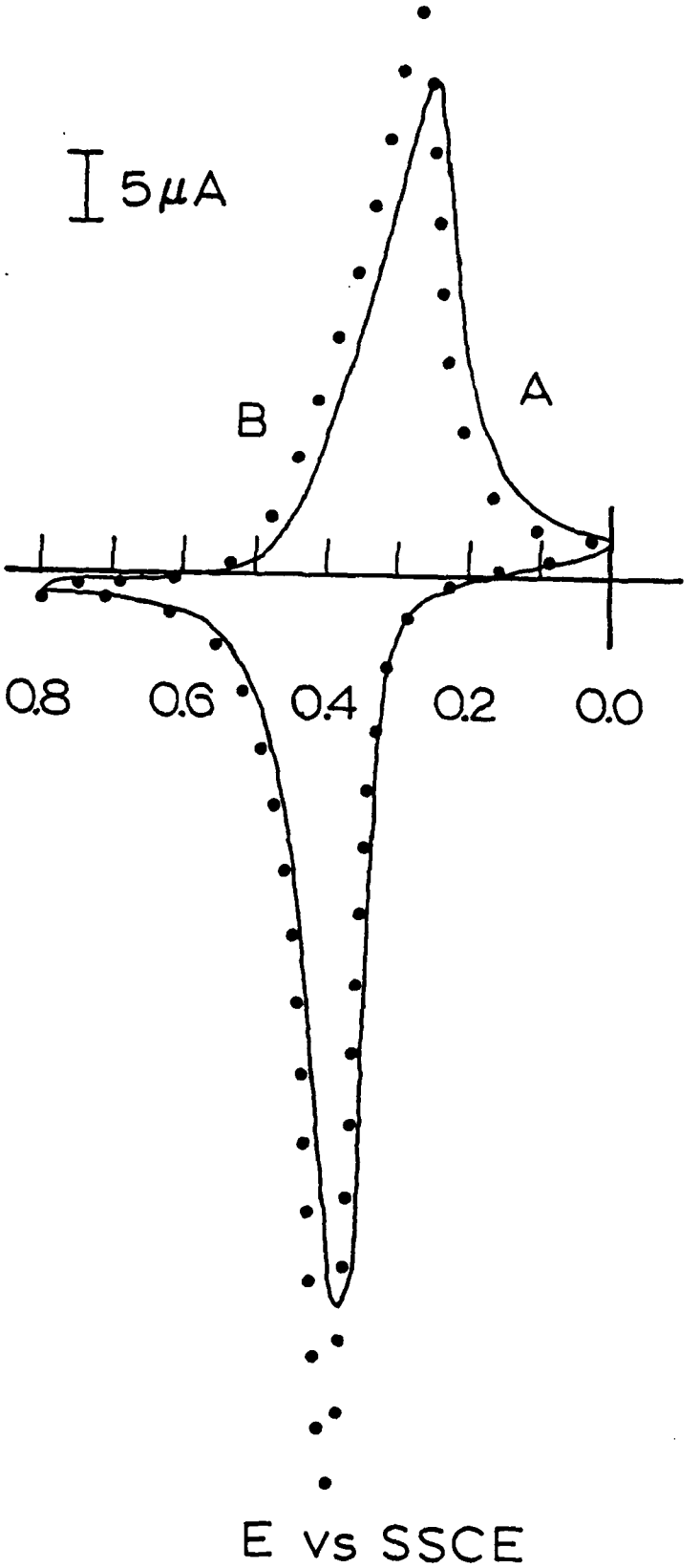

Figure 1

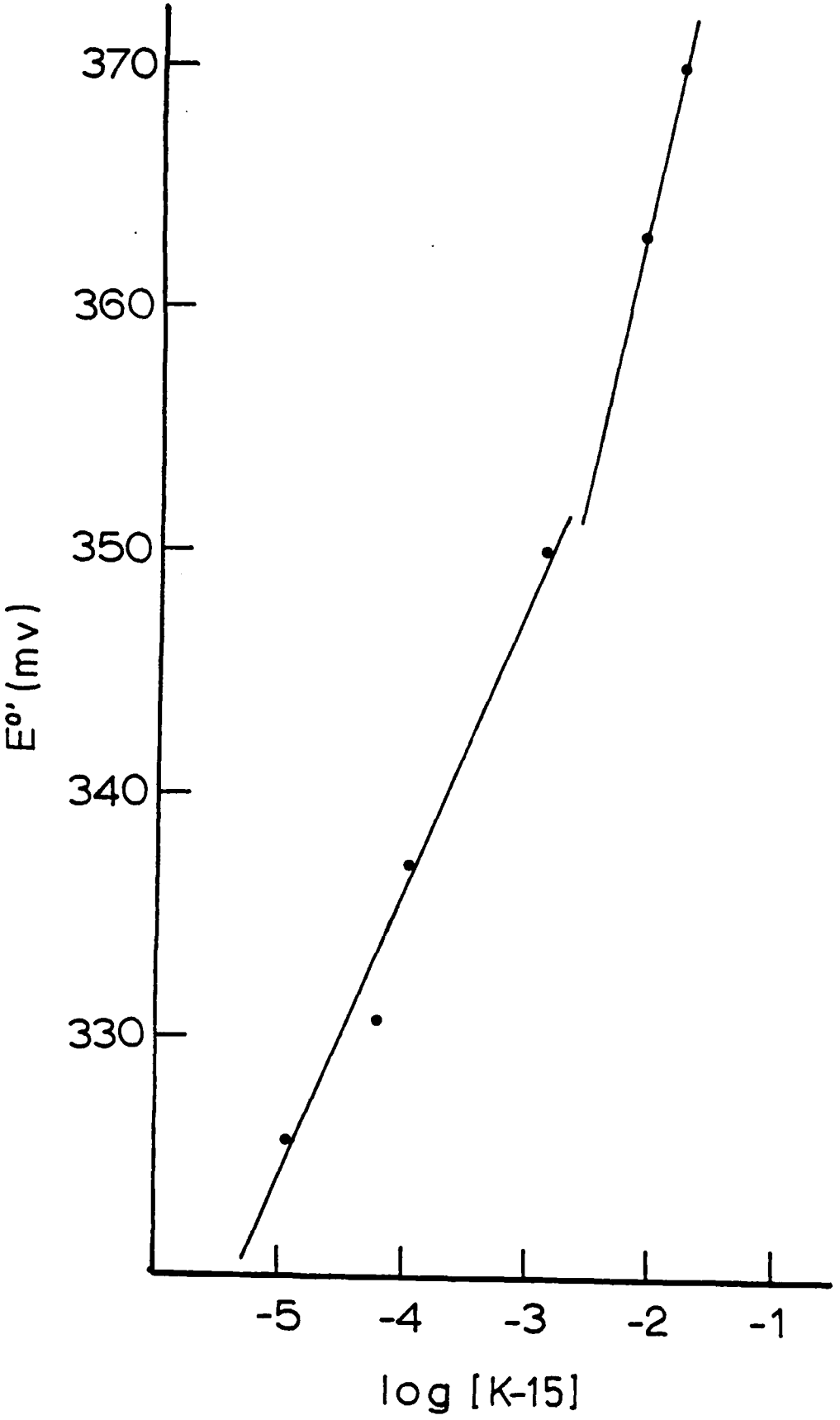

Figure 2

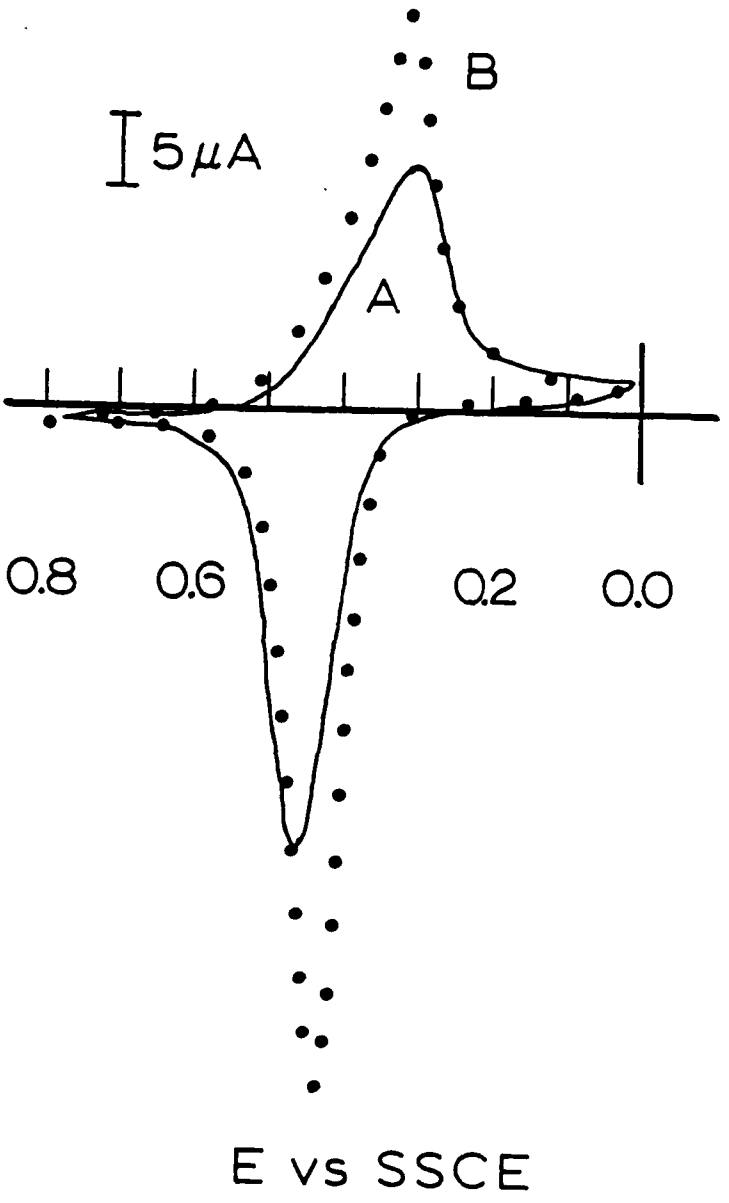

Figure 3

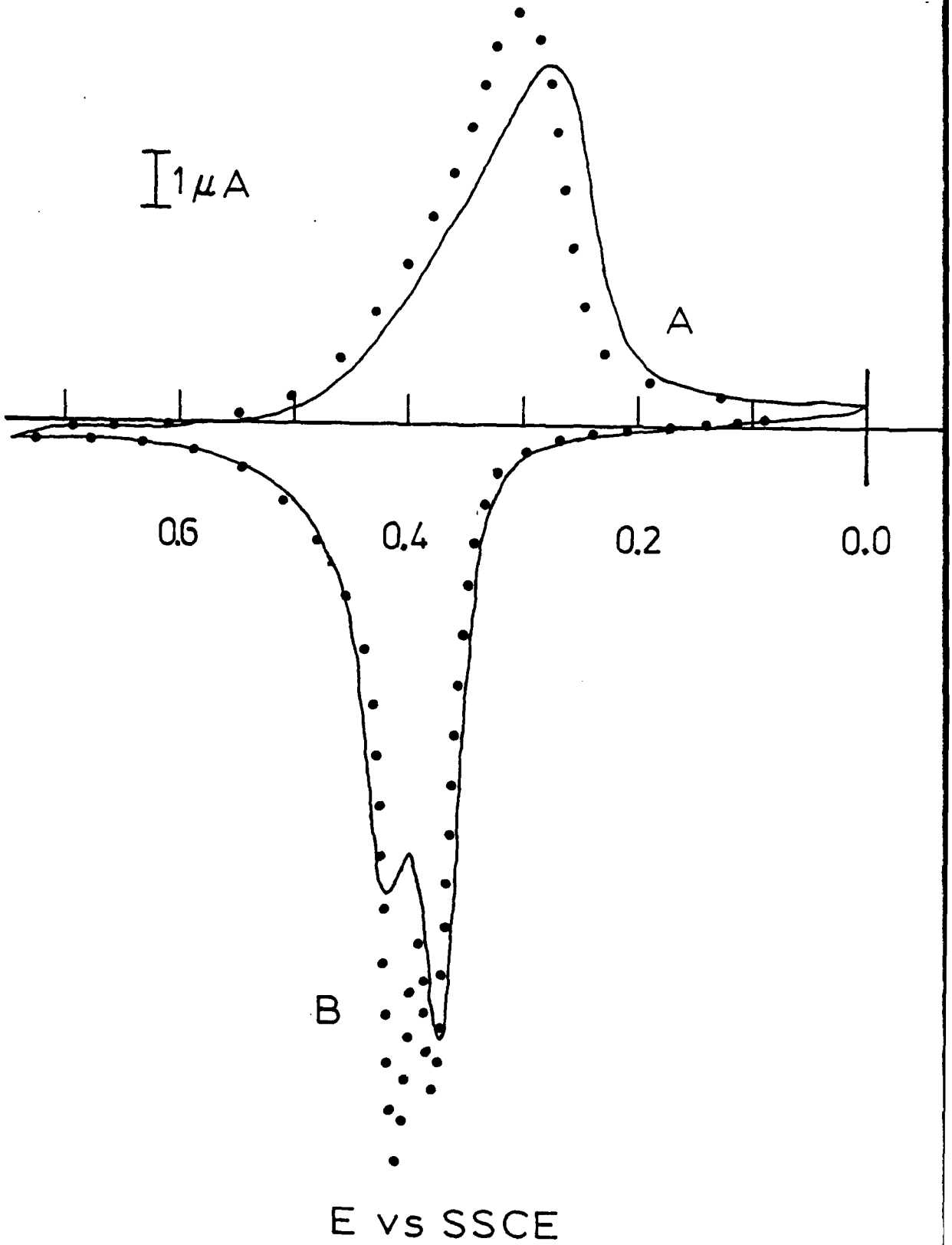

Figure 4

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